EVALUATION OF THE RESULTS OF A ROUND ROBIN ANALYSIS FOR OXYGEN IN POTASSIUM AND SODIUM

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

ABSTRACT

Analysts from 17 laboratories analyzed tube samples of high-purity potassium and sodium for oxygen. Most oxygen analyses were determined by the mercury amalgamation method and several by vacuum distillation; one value of oxygen in potassium was obtained by neutron activation analysis. Analytical results submitted by the participating laboratories gave a mean value for oxygen in potassium of 14.7 ppm with a standard deviation of 5.08 ppm. For sodium, the mean value was 10.7 ppm with a standard deviation of 4.70. The oxygen results for each alkali metal showed variations significantly in excess of the experimental error. Statistical techniques were applied to the oxygen data to identify the most likely sources of variability.

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SUMMARY

A round robin analysis for the determination of low levels of oxygen in potassium and sodium was sponsored by NASA and the AEC. Analysts from 17 laboratories analyzed tube samples of potassium and sodium for oxygen by method(s) and technique(s) commonly used in their respective laboratories. In most instances, the mercury amalgamation method was used to determine oxygen in the alkali metals. Several analysts reported oxygen values that were obtained by use of the vacuum distillation method. One value of oxygen in the potassium was determined by neutron activation analysis.

Analytical results submitted by the participating laboratories gave a mean value for oxygen in potassium of 14.7 ppm with a standard deviation of 5.08 ppm. For oxygen in sodium, the mean value was 10.7 ppm with a standard deviation of 4.70 ppm.

The oxygen data reported for potassium and for sodium showed significant variance in addition to that attributable to experimental error. Analysis of Variance performed on a selected set of results for the same nominal experimental conditions for each alkali metal indicated that for potassium, the major source of variation was attributed to the lack of reproducibility of oxygen analyses within laboratories (statistically referred to as a "block effect"). The major source of variation in the sodium data was attributed to the lack of reproducibility of results among laboratories. The experimental error variances of the selected data for oxygen in potassium and sodium were nearly identical. Other possible sources of variation in the oxygen data did not appear to be significant.

INTRODUCTION

The physical and thermal properties of alkali metals make them attractive as thermodynamic fluids in nuclear turboelectric systems. Experimental tests to select suitable containment materials for nuclear power applications (land based and space) have

focused attention on the necessity of controlling the level of impurities in the alkali metals, especially the oxide concentration. Heat-transfer-loop experiments have shown that a "high" concentration of oxygen in hot, flowing alkali-metal systems can lead to plugging in the cooled tubular loop regions because of the deposition of alkali-metal oxides. Oxide deposition renders that portion of the system useless. This condition is more probable in sodium systems than in potassium systems because of the decidedly lower solubility of the oxide in liquid sodium.

The necessity of controlling the oxide concentration is also important with respect to compatibility. Experiments to evaluate the compatibility of alkali metals and structural materials at high temperatures for extended time periods have shown that corrosion of containment alloys is greatly accelerated when the oxide concentration in the alkali metal is high. For example, corrosion in sodium systems appears to be sufficiently severe in stainless steels at temperatures above 1600° F (1144 K) to demand concentrations of less than 20 ppm oxygen and of less than 10 ppm oxygen for refractory metals in the temperature range of 1800° to 2000° F (1255 to 1366 K) (ref. 1). Because of possible plugging and the corrosion of tube materials, the use of alkali metals for nuclear power Rankine applications may depend to a great extent on the preparation and maintenance of low levels of oxygen in these systems.

Historically, oxygen analyses of alkali metals have been time consuming and difficult to perform and to duplicate. Over the years, many methods have been proposed and tried; some have undergone modifications and others discarded as useless. At present, of the three methods used for the analysis of oxygen in alkali metals, the most widely employed is the mercury amalgamation method. A renewed interest in vacuum distillation, which fell into disfavor, expecially among American analysts, has led to its adoption by a number of laboratories. Both methods involve an acid titration and/or the photometric determination of the alkali-metal ion content of a water solution. This solution contains the basic residue left after the separation process in the mercury amalgamation method or that left after the distillation separation process in the vacuum distillation method. The oxygen concentration in the sample is calculated by assuming that the basic residue, an alkali-metal monoxide, is (depending on the method used) either mercury insoluble or nonvolatile.

A third method, neutron activation analysis, offers a general approach to the analysis of oxygen in some alkali metals. This method, while specific for oxygen, does not distinguish the species of the oxygen compounds that may be present in the alkali metal nor does it distinguish the oxygen in the alkali metal from that of the encapsulating container. Securing a suitable container with a low oxygen background and one that can be filled with the alkali metal and sealed, while preventing contamination, represent major obstacles for the neutron activation analyst.

In 1963, one of the first programs planned to evaluate methods for the analysis of

oxygen in alkali metals was conducted by the NASA Lewis Research Center which initiated a round robin effort for the determination of oxygen in potassium (ref. 2). Eight laboratories participated, each of which was asked to analyze two series of potassium samples for oxygen. The oxygen concentration of one series was low and that of the other was higher. For the low series, three of the participants using the same method (mercury amalgamation) reported values that were in good agreement (about 25 ppm). The results for the high series, however, gave oxygen values that varied widely (from 100 to 1200 ppm). No explanation seemed to account for the large variations. In fact, more questions were raised than answered.

In December, 1964 a steering committee composed of members of NASA and AEC planned an expanded round robin program to determine the oxygen level in both potassium and sodium. About 20 laboratories were asked to participate. The Mine Safety Appliance (MSA) Research Corporation volunteered to supply the alkali metals purified to the oxygen level of interest - about 10 ppm or less. The NASA Lewis Research Center was assigned the task of transferring the potassium and sodium from the MSA commercial containers to sample tubes that were sent to the participants for oxygen analysis. The analytical results were returned to the Lewis laboratory, where the data were tabulated and a meeting of the participants was held in September, 1965 to discuss the results, which are presented in this report.

PURIFICATION OF POTASSIUM AND SODIUM

The alkali metals used for the round robin were designated as high-purity potassium and sodium and, according to the suppliers' analyses, contained less than 10 ppm oxygen.

Potassium

High-purity potassium was prepared from commercial potassium by a distillation process. Commercial potassium, which may contain up to 2 percent sodium and hundreds of parts per million oxygen, is fed into a still on a continuous basis. The still is a 6-inch- (0.1524-m-) diameter stainless-steel column approximately 40 feet (12.19 m) high. The potassium condensate is collected in stainless-steel containers that hold 200 pounds (90.72 kg) of purified potassium. The purity of the product from the still is in excess of 99.99 average percent, with total heavy metal impurities of less than 100 ppm. The sodium content ranges from 10 to 30 ppm and the oxygen, analyzed by the mercury amalgamation method, is usually less than 10 ppm.

The potassium for the round robin was transferred from a 200-pound (90.72-kg) drum to a 10-pound (4.54-kg) container. Because of potential contaimination during the

transfer from the larger to the smaller container, the alkali metal was further purified with respect to its oxygen content by means of hot gettering. About 1/2 pound (0.227 kg) of zirconium chips was added to the 10-pound (4.54-kg) container which was charged with potassium and pressurized to 10 psig (6.895 N/cm^2 gage) pressure with high-purity argon. Hot trapping was performed at 1200° F (922 K) for 24 hours. Alkali-metal samples were extracted directly from the container for oxygen analysis.

Sodium

High-purity sodium was prepared from the distillation of the reactor-grade sodium. As with the potassium, additional purification involved hot trapping in the shipping container under argon gas pressure with zirconium used as the gettering material.

PRELIMINARY OXYGEN ANALYSES

The 10-pound (4.54-kg) containers of potassium and sodium were shipped to the Lewis Research Center from the supplier. According to MSA, three samples each of potassium and sodium extracted from the containers had average oxygen values of less than 10 ppm.

Increased confidence in the low oxygen content of the alkali metal and testing of the transfer and handling procedures were achieved by setting up a small rig in a vacuum chamber to effect the transfer of each alkali metal to several sample tubes for preliminary oxygen analysis. Six sample tubes of potassium and six of sodium were filled and sealed with a compression-type fitting. Three tubes of each metal were sent to the MSA Research Corporation for oxygen analysis, and the remaining tubes were analyzed at Lewis. The preliminary oxygen results from these analyses (all performed by mercury amalgamation method) were in good agreement. The potassium had an average oxygen content of about 11 ppm and the oxygen in sodium averaged less than 10 ppm. The oxygen values were not considered to be significantly different from the initial oxygen results cited in the correspondence from the MSA Research Corporation, which indicated that each alkali metal was homogeneous with respect to its oxygen content and that no appreciable oxygen contamination resulted during the transfer and subsequent handling.
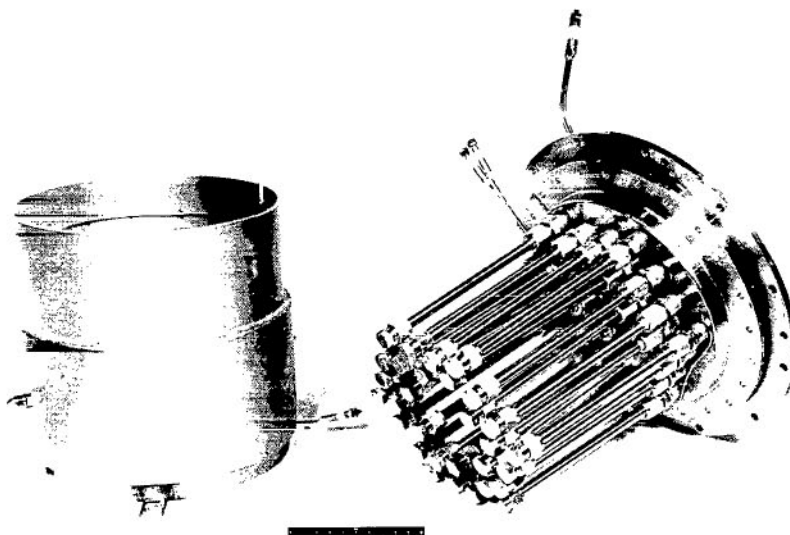
ALKALI-METAL TRANSFER APPARATUS

For the round robin analysis, the transfer of the alkali metal from the commercial container to sample tubes was performed in a vacuum chamber. The 10-pound (4.54-kg)

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container of alkali metal, mounted outside the vacuum chamber, was connected to the alkali-metal distributor mounted inside by means of a 1/4-inch (0.635-cm) stainless-steel transfer line that passed through the vacuum chamber side wall. Swaged heaters or heating tape covered the external surface of the transfer line from the alkali-metal container to the distributor. Chromel-Alumel thermocouples were attached to the transfer apparatus at strategic locations to monitor temperatures.

The stainless-steel distributor, the essential part of the transfer apparatus, is the device that distributes the alkali metal to the individual sample tubes. The assembled distributor contains 30 3/8-inch- (0.95-cm-) diameter tubes and nine 1/2-inch- (1.27-cm-) diameter tubes (the two tube sizes were used for the convenience of the participating laboratories). The sample tubes containing potassium were $6\frac{3}{4}$ inches (17.14 cm) long, and those containing sodium were $8\frac{3}{4}$ inches (22.22 cm) long. The assembled distributor with sample tubes attached and the cylindrical can heater are shown in figure 1. An overflow cup attached to the alkali-metal outlet (not shown in the figure) provided a means to indicate when the sample tubes had been filled during transfer.

Cleanliness of all the transfer components was emphasized to minimize contamination of the alkali metal. All metal surfaces were carefully polished, degreased, and sonically cleaned. White gloves and a special set of clean tools were used to assemble or disassemble all components of the transfer apparatus that were subjected to the vacuum environment. The assembled transfer rig was left overnight under vacuum with moderate heat for outgassing the transfer apparatus and sample tubes.

C-66-3321

Figure 1. - Distributor with sample tubes attached and cylindrical can heater.
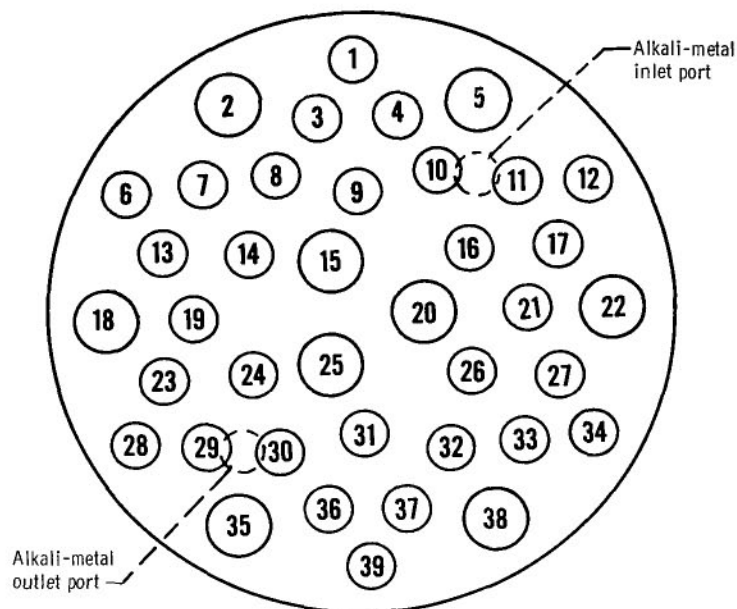
ALKALI-METAL TRANSFER

The next day, with temperatures along the transfer system adjusted to the desired levels and the pressure in the vacuum chamber at less than 2×10^{-5} torr, the alkali metal was pushed by high-purity argon gas from the commercial container into the distributor section and finally into the sample tubes. The transfer progress was evidenced by observing the gradual loss of back pressure on a sensitive pressure gage that was connected to the commercial alkali-metal container. When the alkali metal appeared in the overflow cup, all sample tubes were assumed to be filled and the flow of alkali metal was stopped.

Cooling of the sample tubes was initiated by passing air through the cooling jacket that surrounds the lower part of the cylindrical can heater. The supply container and its transfer line, however, were kept hot and under low argon gas pressure so that additional liquid alkali metal could be forced into the sample tubes during the cooling and freezing periods. After the alkali metal in the tubes had solidified and cooled to room temperature, the vacuum chamber was back filled with high-purity argon gas, and the sample tubes were detached from the distributor and capped with a compression-type fitting.

All sample tubes were radiographed for porosity and piping. Tests at this Center have indicated that porosity (presence of voids) does not cause sample contamination. However, alkali-metal sample tubes with piping, when exposed to an impure gas environment, do reflect oxygen contamination even though the exposed sample ends are discarded. Consequently, all sample tubes that gave evidence of piping were rejected.

The sample tubes were numbered according to the positions shown in figures 2 and 3. The potassium and sodium samples were designated as the P and Q series, respectively.

The round robin samples were checked by additional oxygen analyses performed at Lewis (designated as laboratory O), and the results are presented in figures 2 and 3. The oxygen content of the potassium and sodium (determined by the amalgamation and vacuum distillation methods) averaged 10 and 7 ppm, respectively. These analyses indicated that the potassium and sodium samples were homogeneous within as well as between samples. Since these results were in good agreement with the preliminary oxygen data, the round robin samples were packaged and shipped to the participating laboratories for oxygen analysis.

Figure 2. – Sample tube location on distributor and laboratory analyses for oxygen in potassium (P-series).

Tube	Laboratory	Oxygen analysis, ppm	Tube	Laboratory	Oxygen analysis, ppm	Tube	Laboratory	Oxygen analysis, ppm
1	A	15, 13, ^{a}34, ^{a}30	14	E	^{a}38, 19	27	S	15, 18, 16
2	G	No data reported	15	(b)	(b)	28	K	10, 8, 8, ^{a}15
3	H	^{a}30, ^{a}62, ^{a}20, ^{a}37	16	O	12	29	H	18, 18, 15, 17
4	S	18, 15	17	(b)	(b)	30	T	9, 14, 11, 15
5	Q	12.1, 13.5, 12.1	18	J	12, 12	31	O	8, 8
6	R	14, 16, ^{a}41	19	D	10, 7, 10	32	R	23, 18, 23
7	I	17, 22, 18	20	P	13	33	B	14, 30, 16, 11
8	F	20, 23, 22, 24, 22, 23	21	A	^{a}37, ^{a}46, ^{a}35, ^{a}34	34	F	16, 14, 15, 17, 15, 16
9	N	14, 9, 16	22	(b)	(b)	35	C	10, 12, 6
10	O	11	23	I	22, 14, 11	36	N	4, 4, 8
11	M	No data reported	24	M	No data reported	37	D	24, 22, 23
12	K	9, 8, 10, ^{a}15	25	(b)	(b)	38	L	15
13	T	14, 12, 12, 16, 15, 15	26	O	No data reported	39	E	23, 26

^{a}Value reported by analyst as doubtful.

^{b}Tube sample rejected.

Tube	Laboratory	Oxygen analysis, ppm	Tube	Laboratory	Oxygen analysis, ppm	Tube	Laboratory	Oxygen analysis, ppm
1	L	No data reported	14	B	11, 12, 32, 11, 10, 11	27	B	No data reported
2	K	No data reported	15	(b)	(b)	28	M	No data reported
3	E	[a]23	16	G	11, 15, 16, 17	29	O	6, 5, 6
4	R	31, 31, 23	17	A	20, 15, [a]33, [a]32, [a]30	30	S	12, 11, 5
5	J	4, 4	18	C	4, 6, 5, 5, 7	31	G	[a]33, [a]55, [a]28, [a]35
6	I	8.4, 11	19	D	8, 7, 7	32	E	17
7	O	10, 6, 10	20	P	1	33	F	8, 9, 8, 8, 7, 8
8	P	3	21	O	No data reported	34	L	No data reported
9	T	15, 14, 18, 13, 14, 14, 16, 16	22	H	No data reported	35	K	No data reported
10	N	8, 39, 6	23	I	14, [a]35	36	N	No data reported
11	S	7, 9, 7	24	A	20, 13, 17, 16, 20	37	T	16, 17, 17, 18, 17, 16
12	M	No data reported	25	(b)	(b)	38	Q	14.2, 14.0, 13.5
13	F	12, 10, 11, 11, 11, 8	26	R	49, 50, 58, 56	39	D	4, 4, 5

[a]Value reported by analyst as doubtful.

[b]Tube sample rejected.

Figure 3. – Sample tube location on distributor and laboratory analyses for oxygen in sodium (Q-series).

GENERAL VARIABILITY OF OXYGEN DATA

Figures 2 and 3 indicate the position of the potassium and sodium sample tubes on the distributor relative to the alkali-metal inlet and outlet ports. Also shown are the sample tubes that each laboratory received and the oxygen results they reported. Tables I and II summarize the analytical data, giving the sample weight, the oxygen values reported, brief statements about the method of analysis, and experimental conditions under which the analyses were conducted.

The oxygen data presented in this report are those which the analysts submitted. In some cases the data were corrected for blanks, and in other cases it was not clear that a blank was determined or used. In this evaluation, no distinction was made between corrected and uncorrected data; however, a brief discussion of the importance of the oxygen blank is given in the section DISCUSSION OF OXYGEN BLANK.

In tables I and II, certain oxygen results are marked with a superscript "a", designating that the analyst believes them to be in error. Consequently, these values, although shown in the two figures and tables, were not used in the present evaluation of the round robin data.

Examination of the oxygen data in figures 2 and 3 revealed that, from supposedly homogeneous alkali-metal samples, the oxygen results for potassium and sodium varied considerably. For example, oxygen values ranged from 4 to 26 ppm for potassium and from 3 to 58 ppm for sodium. On the one hand, analyses from sample tubes in a given distributor location showed excellent agreement with analyses in different distributor locations (cf. in fig. 2, potassium samples P-5 and P-35; in fig. 3, sodium samples Q-5, Q-18, and Q-33). On the other hand, tube analyses in a given distributor location may differ widely from others in the same general area (cf. in fig. 2, potassium samples P-36 and P-37; in fig. 3, sodium samples Q-4 and Q-5).

A more detailed examination of the data in figures 2 and 3 revealed that, in general, a higher degree of precision existed for the within-tube oxygen analyses than for the collective-tube analyses. For example, analyses from potassium tubes P-8 and P-37 (fig. 2), each giving a mean value of about 22 ppm oxygen, showed a high degree of internal precision even though the tubes were located in different sectors of the distribution field. In the vicinity of tube P-8 are P-9, P-5, and P-13, each with a mean value of about 13 ppm oxygen. Precise results were obtained for the tubes surrounding P-37: the mean values for oxygen content were 15.5 ppm for P-34, 8 ppm for P-31, and the single value of 15 ppm for P-38.

The high degree of precision in within-tube analyses was evident from similar comparisons made of the data in figure 3. In the area of Q-9, which has a mean value of 15 ppm oxygen, are tubes Q-7 and Q-11 with mean values of 9 and 8 ppm, respectively.

Likewise, in the vicinity of tube Q-37, with a mean value of 17 ppm, is Q-38, mean value of 14 ppm, and Q-33, mean value of 8 ppm.

The examples cited (and there are others) show that the analysis for a given tube on the distributor is in good agreement with those of others in its immediate vicinity and is in agreement with tube analyses distant from it. The examples also reveal that tube analyses can differ greatly, even when the sample tubes are located in the same distributor area. These general observations suggest that no obvious location patterns exist which can account for the variations in oxygen content in either potassium or sodium. However, such variations in the oxygen data do raise many questions concerning sample homogeneity and the effect of tube location on the distributor relative to the oxygen content of the samples: Is tube size a factor? Does a sample that is extruded from a tube differ significantly in its oxygen content from a sample that is leached from a cut section of that tube? Questions were also raised concerning the applicability of current methods used for the oxygen analysis of alkali metals as well as those concerning the analytical environments.

These questions and others plagued the analysts in the previous round robin effort, and for the most part, no adequate answers could be given. In this round robin, sufficient data were available to permit a limited statistical analysis, which made it possible to evaluate the effect of several analytical factors and to suggest answers to some of the questions.

PRELIMINARY EVALUATION OF OXYGEN DATA

Before the statistical calculations are discussed, a consideration given to some of the reported data should be noted. Certain values reported for oxygen in sodium deviated by as much as 6 standard deviations from the group average, but they were not designated by the analyst as being questionable (oxygen results from tubes Q-4 and Q-26). These values and the single values of 32 ppm from Q-14, 39 ppm from Q-10, and 30 ppm from P-33 were assumed to be outliers and were rejected from further consideration.

Statistics were applied to the data to determine the frequency distribution of the individual values (excluding those outliers just discussed) for oxygen in potassium and sodium. The results are shown as histograms in figures 4 and 5. Superimposed on the histograms are the normal frequency curves that one would expect for the same number of observations for each case based on the same mean and standard deviation as the given data (ref. 3).

The mean of the individual values for oxygen in potassium is 14.7 ppm with a standard deviation of 5.08 ppm. For oxygen in sodium, the mean of the data is 10.7±4.70 ppm. These standard deviations are the square roots of their respective error variances of 25.81 and 22.09.
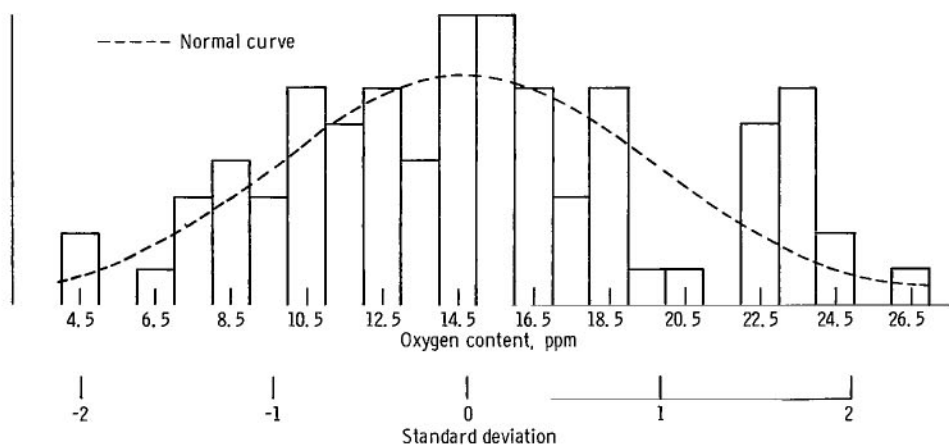
Figure 4. - Distribution of results for oxygen in potassium. Number of analyses, 81; mean of data, 14.7 ppm oxygen; standard deviation, 5.07 ppm oxygen.
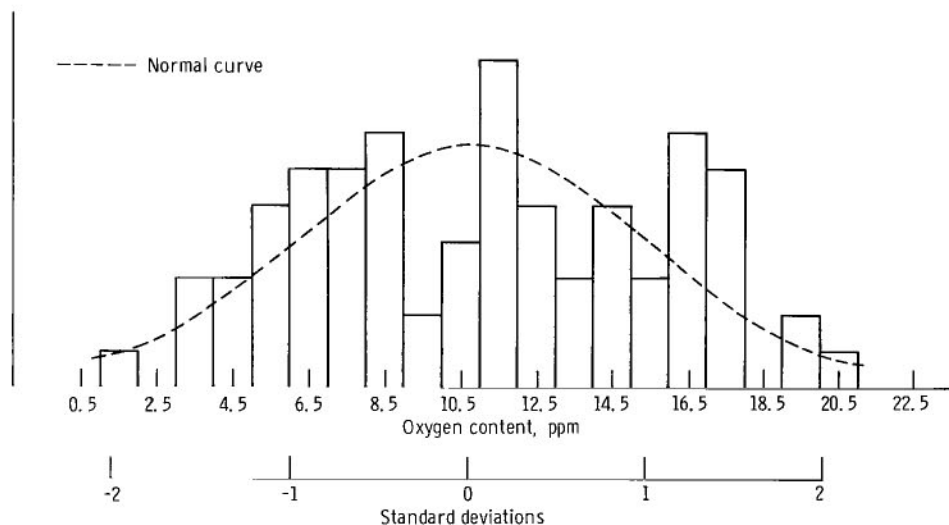
Figure 5. - Distribution of results for oxygen in sodium. Number of analyses, 78; mean of data, 10.7 ppm oxygen; standard deviation, 4.70 ppm oxygen.

The replication error variance can also be calculated for each metal with data from each laboratory where more than one analysis was performed on each sample tube using the same technique. These are true replicates and differ only in sample weight (although they may represent different positions along the tube). The sample weight is assumed to have no effect on the analyses within the range it varied for each tube. The replication error variance was 2.47 for sodium with 52 degrees of freedom and 4.66 for potassium with 50 degrees of freedom. A single-tail F-test (ref. 3) was performed for each metal to determine if the overall variance for each metal distribution was significantly greater than its respective replication error variance. For sodium, this ratio was 7.36, which

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was significant to less than a 0.1-percent level for the 71 degrees of freedom in the numerator and the 52 degrees of freedom in the denominator. For potassium, this ratio was 5.54 for 80 degrees of freedom in the numerator and 50 degrees of freedom in the denominator. Again, the ratio was significant to less than a 0.1-percent level for the degrees of freedom involved. These F-ratio values mean that the chance that these ratios could have occurred randomly is less than 1 in 1000.

These preliminary results imply that there are significant source(s) of variation adding to the experimental error variance. Since this preliminary analysis of the oxygen data suggested the presence of other sources of variation besides experimental error, it seemed reasonable to try to isolate first and then evaluate these sources by some appropriate statistical procedure.

POSSIBLE SOURCES OF VARIATION IN OXYGEN DATA

Sources of variation were assumed to be of two different types: (1) those due to differences in the alkali-metal samples, and (2) those due to differences in the analytical technique. In an ideal case, if all experimental factors could be held invariant, the test results for a given metal would be the same except for the error due to replication (experimental error). In this real case, however, the isolated factors plus the replication error would account for nearly all the total variation (i.e., total sums of the squares).

Variation Due to Sample

The first sample factor considered was the radial distance of the sample tube from the alkali-metal inlet port. This factor could not be satisfactorily isolated because each radial distance is represented by a given tube, which, when analyzed for oxygen, was treated as an individual block or batch. Consequently, any effect of distance on sample homogeneity was confounded by the tube block (or batch) effect and thus could not be isolated.

The second possible source of sample variability considered was inhomogeneity within a tube - sample variability lengthwise in a tube as well as radial inhomogeneity. Although the data were inadequate to determine the existence of radial oxide segregation, there is no reason to believe that oxide segregation existed lengthwise in any of the sample tubes. In general, most oxygen results listed in tables I and II and in figures 2 and 3 were not designated as to position along the sample tube. Five laboratories, however, did designate the sample position along the tubes, and although these data were obtained

from only 19 of the total number of sample tubes in the round robin, no position effect was apparent for oxygen in potassium or in sodium. Therefore, the within-tube variance is believed to be an unambiguous estimate of the experimental error and not evidence of either radial or longitudinal sample inhomogeneity.

A third source of sample variation was tube size. This factor could be isolated and possibly, therefore, lends itself to evaluation.

Variation Due to Method of Analysis and/or Technique

The technique variables considered were (1) whether the tube was cut or the alkali metal was extruded, (2) whether the analysis was performed in an inert gas or vacuum environment, and (3) whether the method used an end-point titration or a flame test. In addition, because six of the 78 sodium analyses were performed by vacuum distillation, whereas all others were analyzed by mercury amalgamation, an attempt was made to determine if the two methods gave significantly different results.

EVALUATION OF PRINCIPAL SOURCES OF VARIATION IN OXYGEN DATA

Application of Regression Analysis to Oxygen Data

Regression analysis was the technique chosen initially (ref. 4) to evaluate the significant factors. Of the five variables selected, only one (tube size) was a sample variable, the others being technique variables. These five variables are qualitative factors, which can be assigned dummy numerical values so that they can be treated quantitatively (ref. 4) in multiple-regression analysis. Because the qualitative factors were all run at two levels, -1 and +1 were chosen for the respective levels, as shown in the following table:

Level	Qualitative factor									
	X_1		X_2		X_3		X_4		X_5	
	Small tube	Large tube	Tube cut	Metal extruded	Vacuum	Inert gas	Titra-tion	End point (flame or atomic absorp-tion)	Mercury amalga-mation	Vacuum distil-lation
-1	✓		✓		✓		✓		✓	
+1		✓		✓		✓		✓		✓

The data were first displayed in factorial form as in tables III and IV. All values run under the same nominal conditions are grouped in one cell. Thirty-two cells were possible for the sodium data and 16 for the potassium. The sodium data occurred in only 10 of the 32 cells, whereas the potassium data occurred in 8 of the 16. For convenience, these cells were designated by Roman numerals. In addition, each cell received letter designations for the laboratories whose individual analyses are listed below a particular tube. The average of all the values in each cell $\overline{Y}_c$ is also listed. Each tube is characterized by a given radial distance and was presumed to have been analyzed separately as time blocks (i.e., the samples were not analyzed concurrently, but at some different point in time).

In an ideal case, the same number of values should occur at each level of a given factor. In tables III and IV, one cell (III, $X_1 = -1$, $X_2 = +1$, $X_4 = -1$ and $X_5 = -1$) has most of the data for both metals.

The factors of interest, and particularly interactions, were difficult to evaluate properly because the data were so badly unbalanced, thereby leaving many empty cells. However, such a statistical layout should permit simple factors to be evaluated by multiple regression. Care must be taken not to estimate too many parameters, since the effective number of data points is eight for potassium (not 81) and 11 for sodium (not 78), based on the number of cells in tables III and IV (ref. 4).

Multiple-linear-regression runs were performed for both sets of oxygen data by using equations of the form $y = a + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_4 x_4 + b_5 x_5$. In general, the goodness of fit of the regression line to the oxygen data was poor, with a large percentage of unexplained variation. Using a more simplified equation of the form $y = a + b_i x_i$, where only two cells or a single factor was involved, resulted in no significantly improved fit.

The two approaches gave analytical results that were ambiguous and often contradictory. To some extent, such results seemed to be caused by inhomogeneities in the replication error variance among cells and, perhaps, by source(s) of variation within the cells not accounted for in the regression analyses. In addition, examination of the data in the individual cells, particularly in cell III, reveals that the range of data for this one cell nearly spans the spread of the data of the remaining cells. This degree of data spread makes comparison between cells (i.e., factors) by regression analysis or by any other statistical approach questionable.

The specific implication from the regression analyses is that some source(s) of variation present within a given cell is significantly greater than the replication error of that cell and therefore masks any differences between cells (i.e., factors). Thus, the logical approach was to go the individual cells to try to determine the source(s) of variation.

Application of Analysis of Variance to Selected Oxygen Data

Attention was focused directly on cell III for both metals where no factors were varied and a large number of data points were available for analysis (25 data points for sodium and 33 for potassium). The question then asked was whether or not significant differences existed among the laboratories in this one cell and/or between tubes (blocks) run by the same laboratory as compared with the variability of the analyses within the tubes. This question was answered by using the statistical technique of Analysis of Variance (ANOVA). This approach partitions the total variability (sum of squares) of the analytical results into (1) variability due to laboratories, (2) variability due to tubes within laboratories, and (3) variability due to differences within a tube (i.e., experimental error). These sums of squares were then divided by their respective number of degrees of freedom to give the corresponding variances or mean squares. The ratio of the proper variances indicated whether or not the factors under consideration (among laboratories and among tubes) were significant.

A schematic nested layout of the data for ANOVA for each alkali metal from cell III is shown in table V. Only the data where more than one tube was run by a given laboratory are listed, which gives a total of 28 values (5 laboratories) for potassium and 17 values (3 laboratories) for sodium. The tubes are nested under each laboratory. The standard ANOVA tables for each alkali metal are given in tables VI and VII. The various values were calculated from the standard technique described by Winer for a nested design (ref. 5).

In table VIII, the tests of significance are performed as indicated in the columns Components of variance or Mean square. First, the tube variance $\sigma_\epsilon^2 + \tilde{n}\sigma_B^2 = MS_{B(A)}$ is compared with the error variance $\sigma_\epsilon^2 = MS_\epsilon$. If this ratio is substantially greater than 1, it implies that the value of $\tilde{n}\sigma_B^2$ is large since the σ_ϵ^2 is effectively the same in both expressions. The question is how large the $MS_{B(A)}$ term must be before its effect would be real and not just chance. This question is resolved by the F-statistic, which is tabulated for the ratio of two variances. This F-statistic is a single-tail F-test because it is based on the probability of the ratio exceeding 1 as determined for the number of degrees of freedom involved. Choosing a 95-percent probability level means that the chance occurrence of a ratio that will exceed the proper F-table listing is less than 5 percent.

A test was conducted to determine if significant differences exist among the results of laboratories in one cell and/or between tubes analyzed by the same laboratory as compared with the variability of the analyses with the tube. The test for the significance of the laboratories $\sigma_\epsilon^2 + \tilde{n}[1-(b/B)]\sigma_B^2 + \tilde{n}b\sigma_A^2 = MS_A$ depends on the value of the sampling factor b/B. If $b/B \to 0$, the so-called random case is indicated in which only a small fraction of a population is sampled; if b/B is 1, the entire population is sampled, and the fixed case is indicated. In this study, b/B was assumed to be zero for purposes of

generalization. This assumption means that the significance of the laboratory is tested against the block effect $MS_A/MS_{B(A)}$ with the proper number of degrees of freedom.

For both alkali metals, the tube error is about the same, as shown in tables VI and VII. For sodium, all the significant variability results from differences among laboratories, whereas for potassium, the variability among tubes (block effect) is large enough to overshadow any differences among analysts (i.e., among laboratories). A block effect, as shown by potassium, implies that a given laboratory could not duplicate its analytical conditions from one run to the next: slight differences in experimental conditions have a greater effect on potassium oxygen results than on sodium results. Thus, the variability of tube analyses within laboratories observed for potassium and not for sodium is consistent with the greater chemical reactivity of potassium compared with that of sodium. A laboratory difference implies that two or more laboratories supposedly performing analyses under the same conditions (i.e., the same cell in this investigation) actually differed significantly in some unknown manner. For potassium, this additional variability raised the standard deviation on the estimate of the cell mean from 2.14 to 5.59 ppm, whereas this standard deviation for sodium was raised from 2.15 to 5.24 ppm.

EVALUATION OF OTHER SOURCES OF VARIATION

Comparisons of the various cells to derive the effect of other sources of variation, such as tube size, removal method, analytical environment, and radial distance from the inlet, can only be made in a general way by comparing the cell mean values in tables III and IV. For example, comparing cells I and II for sodium shows no real effect of the method of removal. On the other hand, comparing cells II and III for potassium does show an apparent environmental effect. Also, large tubes in general had lower oxygen values than those of small tubes. However, because either the laboratory or the tube effects were so strong and most cells did not have even one laboratory in common, such comparisons are probably misleading.

A valid comparison can be made between cells to determine the effect of the method of removal (end-point determination X_4) based strictly on values of laboratory T from cells III and V for each alkali metal (since each sample was split). A regression analysis of the two cells with the model $Y = a_1 + b_4 X_4$ showed that b_4 was not significant for either metal to the probability level 0.95.

A comparison was made from sodium data to determine whether the mercury amalgamation method differed significantly from the vacuum distillation method. Tube Q-24 (see fig. 3) was split into 5 samples, two of which were analyzed by mercury amalgamation (cell III, laboratory A) and gave values of 19.7 and 12.6 ppm. The remaining three samples were analyzed by the vacuum distillation method (cell X, laboratory A) and the

reported values were 16.5, 16.1, and 20 ppm. A t-test performed on the two means was not significant at $\alpha = 0.05$. Laboratory O also analyzed two other tubes using two different methods: vacuum amalgamation for one tube (Q-7, cell IX) and vacuum distillation for the second tube (Q-27, cell IX). Again, the differences in the means of the tubes (9 and 6 ppm oxygen, respectively) are not considered significant. In figure 2, the single value of 15 ppm obtained by neutron activation analysis is in good agreement with other analyses for oxygen in potassium. These comparisons of oxygen values by the methods of analysis are in agreement with the results of an independent study in which the methods of mercury amalgamation, vacuum distillation, and neutron activation were compared (ref. 6).

The assumption that the radial distance from the alkali-metal inlet to a given tube was not a significant factor was substantiated by laboratory T's data in cell III for both metals (tables III and IV). For sodium, the radial distances of tubes Q-9 and Q-37 (table IX) were 4.9 and 13.5 centimeters, respectively, with no real difference in the two analyses. However, for potassium, tubes P-13 and P-30, the two distances were 12.4 and 13.3 centimeters, respectively, with perhaps a 2-ppm difference between tubes. Another example, for sodium in cell III (table IV, tube Q-8), is the value given by laboratory P as 3 ppm at a distance of 7.8 centimeters. For this same cell, laboratory A ran two tubes, one at 4.0 centimeters (Q-17) and the other at 11.8 (Q-24) and gave values that averaged 17.3 and 16.1 ppm, respectively. Such comparisons reinforce the contention that radial distance was not a significant factor.

DISCUSSION OF OXYGEN BLANK

An area in the analysis of alkali metals for oxygen content that generally has not been given sufficient emphasis is the determination of an oxygen blank. Alkali metals, being extremely reactive substances, readily react with residual oxygen, carbon dioxide, and water vapor in vacuum environments and in inert gas atmospheres, and react with carbonates, moisture, and oxygen impurities in chemical reagents and on the surface of the analytical apparatus. Depending on the environment and experimental practices, the magnitude of a blank may range from a few micrograms of oxygen to a value large enough to equal or exceed the amount of oxygen sought in a given alkali-metal sample.

In only a few cases did the analysts perform their analyses so that a blank could be determined. Where the data permitted - that is, where the analyst significantly varied the weights of the alkali-metal samples - total micrograms of oxygen were plotted against sample weight. Such a plot is expected to yield a linear relation, and extrapolation of the curve to zero sample weight gives the blank correction.

Plots of total oxygen against sample weight from data submitted by several laboratories are shown in figures 6(a) to (e) for oxygen in potassium and in figures 7(a) to (f)

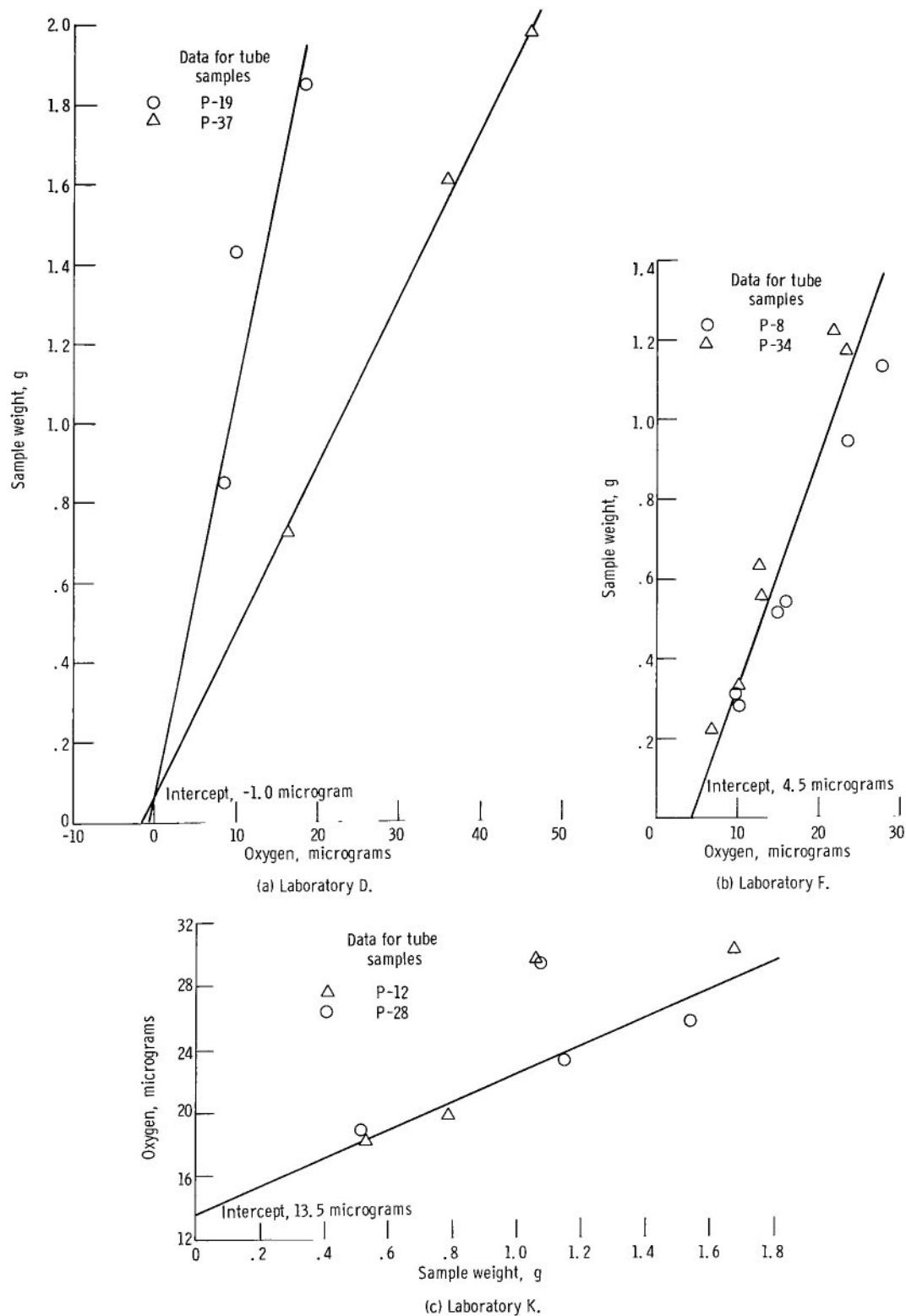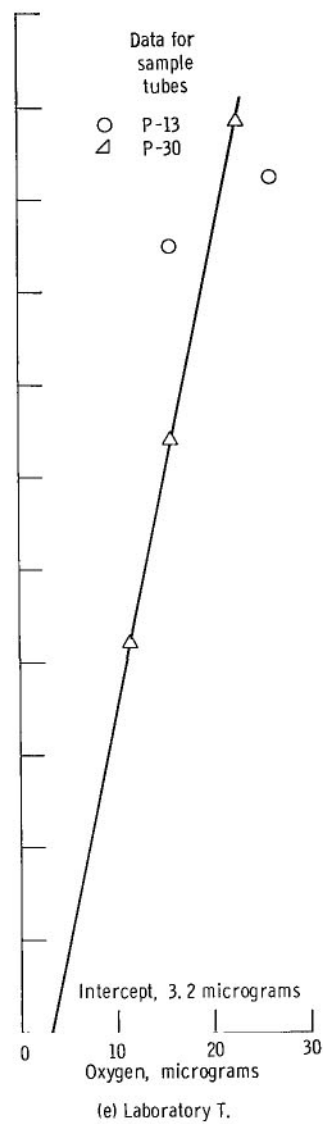Figure 6. - Estimate of oxygen blank in data for oxygen in potassium.

(d) Laboratory R.
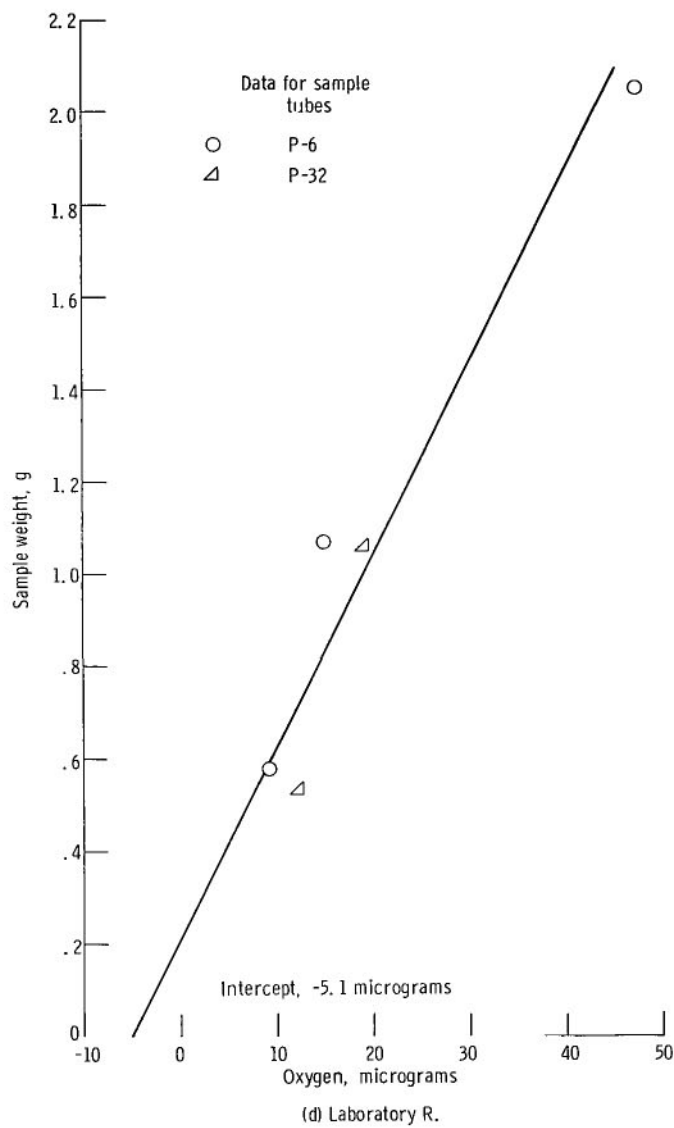
(e) Laboratory T.
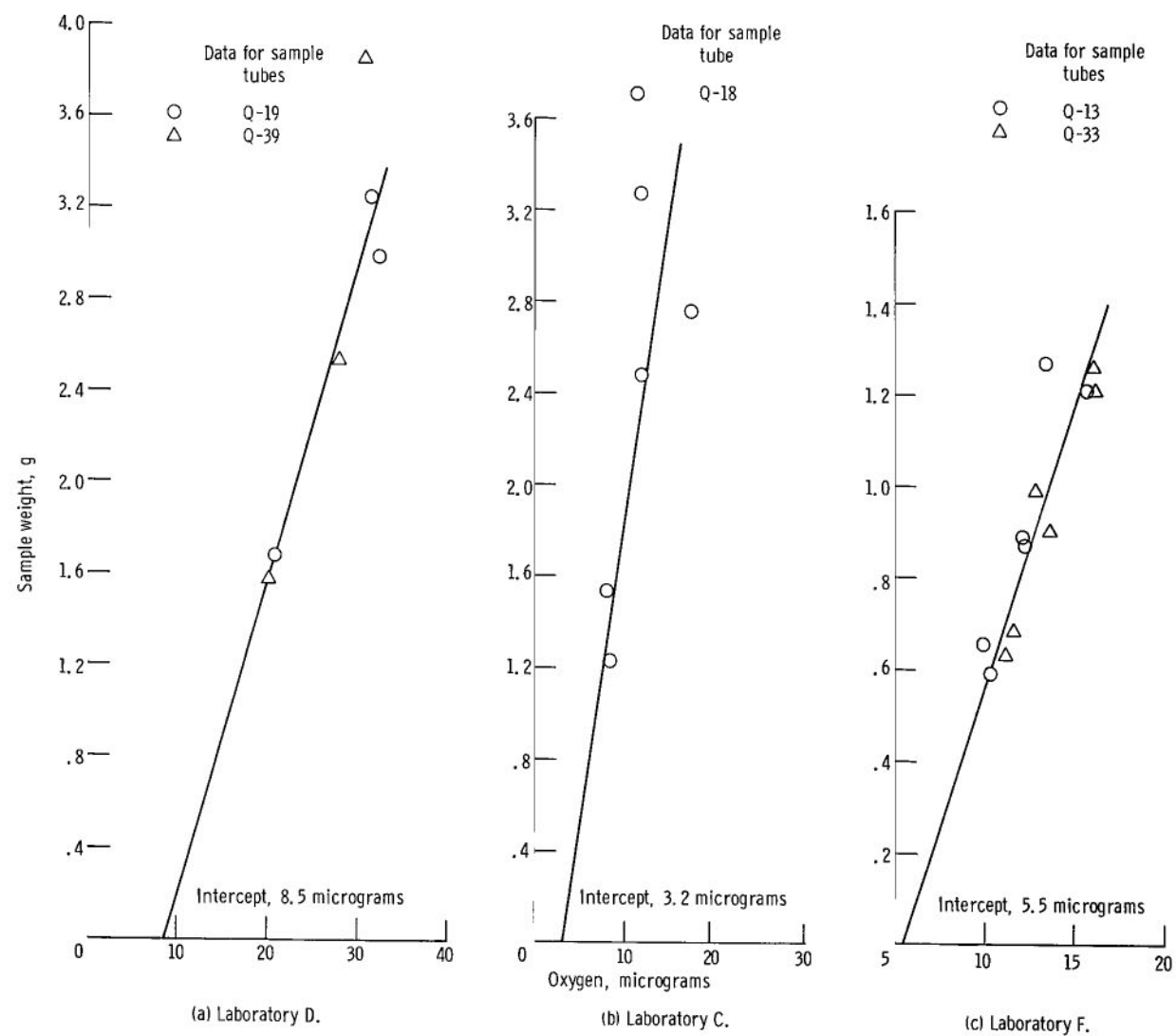
Figure 6. – Concluded.

Figure 7. – Estimate of oxygen blank in data for oxygen in sodium.
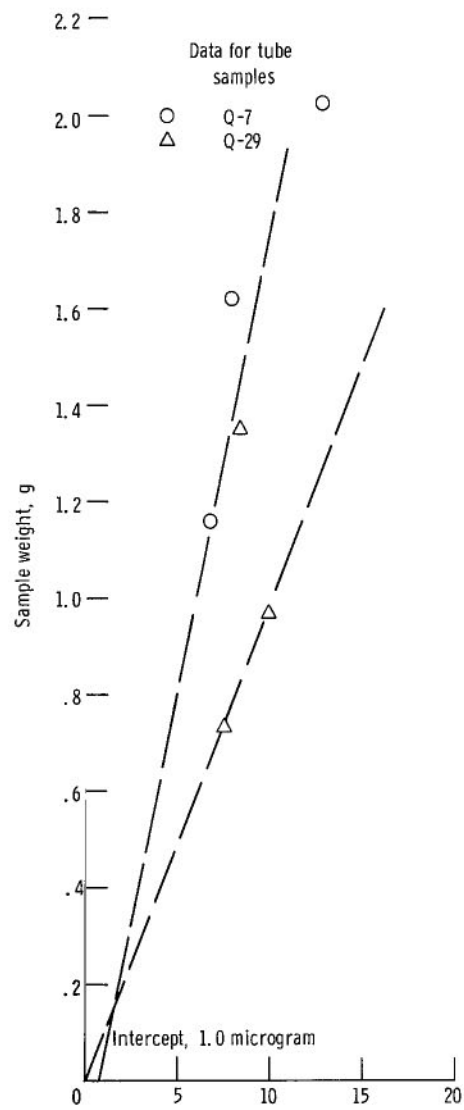
(d) Laboratory O.
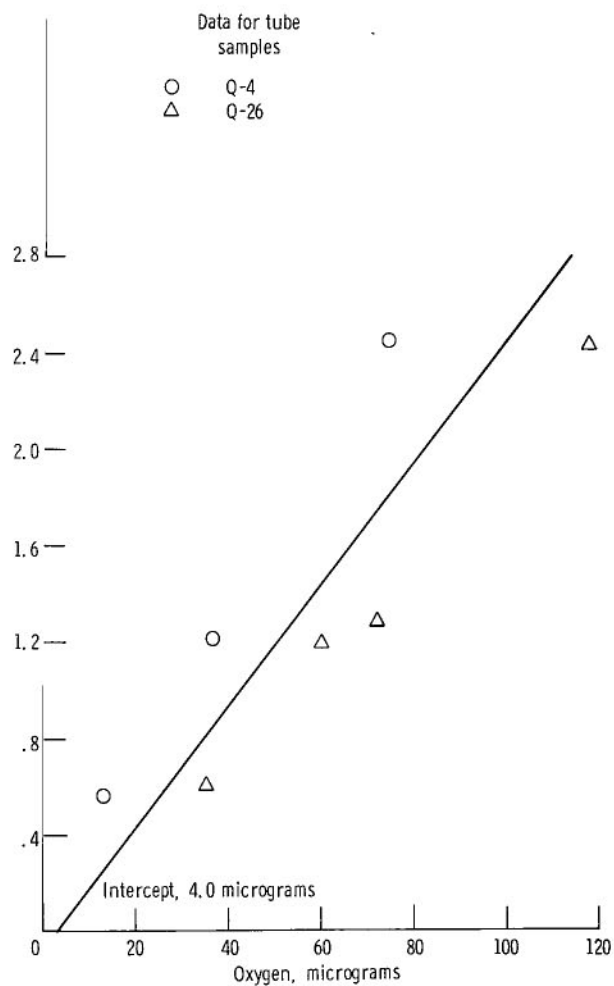
(e) Laboratory R.
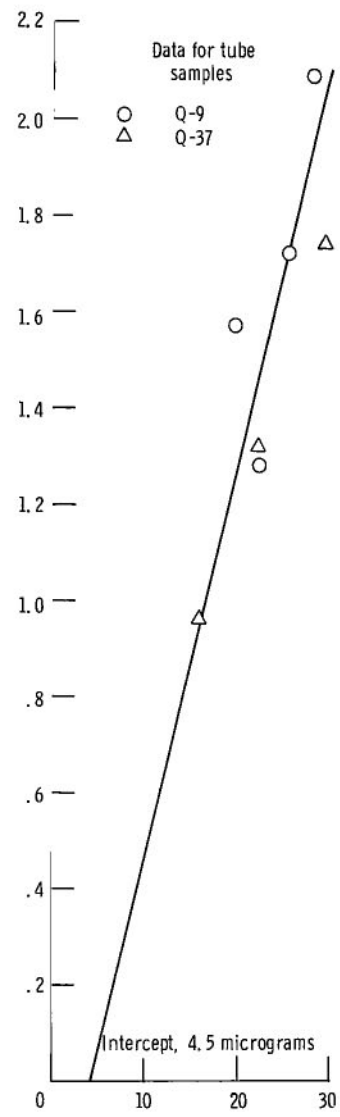
(f) Laboratory T.

Figure 7. – Concluded.

for oxygen in sodium. Inspection of these plots shows the blanks, in most cases, to be small - about 4 micrograms of oxygen. In two cases, however, large blanks are obtained and in two other cases, the blanks have negative values.

Although these plots are important to obtain an estimate of the magnitude of the blank correction to apply to calculations for oxygen, they serve an additional function. At least qualitatively, they are a measure of the internal consistency and precision of the oxygen analyses. The degree to which a total oxygen sample-weight plot adheres to a straight line to yield a small blank estimate reflects how well the analyst was able to control the environmental variables inherent in the analytical methods for oxygen in the alkali metals. Therefore, oxygen blank determination, calculated from multiple sample weights, is recommended as one of the ground rules for any future round robin effort.

SUMMARY OF RESULTS

An analytical round robin, performed on single batches of samples of high-purity sodium and potassium to determine the level of oxygen impurities, gave the following results:

1. The average oxygen values derived from the results of 17 participating laboratories were 14.7 and 10.7 ppm oxygen, respectively, for potassium and sodium with respective standard deviations of 5.08 and 4.70 ppm.

2. The overall variances for the oxygen data, when compared with the experimental error for each sample tube, indicated significant source(s) of variation in addition to the experimental or random error.

3. The statistical technique of analysis of variance (ANOVA) performed on a selected set of data identified the major sources of the variation. For sodium, all the significant variability resulted from differences among the laboratories, whereas for potassium, significant variability resulted from the lack of reproducibility within laboratories. These findings are consistent with the greater chemical reactivity of potassium, as compared with that of sodium, and indicate the greater sensitivity of potassium to small differences in environment.

4. Factors that might influence sample homogenity, such as radial and longitudinal oxide segregation in the tube and radial and longitudinal distance from the alkali-metal inlet, were not considered significant.

5. Analytical factors, such as the overall method (mercury amalgamation, vacuum distillation, and neutron activation) and the method of end-point determination (titration and flame, or atomic absorption), showed no significant effect on the oxygen analyses. The method of removing the sample from the tube (tube cut or metal extruded) and the

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environment of the separation (vacuum or inert gas) could not be compared on a rigorous basis but appeared to be only slightly significant, if at all.

Lewis Research Center,
    National Aeronautics and Space Administration,
        Cleveland, Ohio, September 24, 1968,
            129-03-03-01-22.

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Laboratory	Sample tube	Sample weight, g	Oxygen, ppm	Analytical method		Analytical environment
				End-point determination of potassium oxide	Separation	
A	P-1	1.15	15.4	Potentiometric titration	Amalgamation	Argon gas atmosphere
		1.22	13.0	Potentiometric titration	Amalgamation	Argon gas atmosphere
		1.24	[a]33.9	Potentiometric titration	Vacuum distillation	Vacuum, 2×10^{-6} torr
		1.29	[a]29.9	Potentiometric titration	Vacuum distillation	Vacuum, 2×10^{-6} torr
	P-21	1.28	[a]36.8	Potentiometric titration	Amalgamation	Argon gas atmosphere
		1.23	[a]45.5	Potentiometric titration	Amalgamation	Argon gas atmosphere
		1.21	[a]35.1	Potentiometric titration	Vacuum distillation	Vacuum, 2×10^{-6} torr
		1.23	[a]33.8	Potentiometric titration	Vacuum distillation	Vacuum, 2×10^{-6} torr
B	P-33	1.35	14	Indicator titration	Amalgamation	Monitored helium gas atmosphere
		1.23	30			
		1.11	16	↓	↓	↓
		1.13	11			
C	P-35	2.71	10	Flame photometry for potassium	Amalgamation	Recirculating argon gas atmosphere
		1.15	12	Flame photometry for potassium	Amalgamation	Recirculating argon gas atmosphere
		2.71	6	Flame photometry for potassium	Amalgamation	Recirculating argon gas atmosphere
D	P-19	0.848	10	Indicator titration	Amalgamation	Monitored argon gas atmosphere
		1.431	7	Indicator titration	Amalgamation	Monitored argon gas atmosphere
		1.853	10	Indicator titration	Amalgamation	Monitored argon gas atmosphere
	P-37	0.725	24	Indicator titration	Amalgamation	Monitored argon gas atmosphere
		1.611	22	Indicator titration	Amalgamation	Monitored argon gas atmosphere
		1.975	23	Indicator titration	Amalgamation	Monitored argon gas atmosphere
E	P-14	1.02	[a]38	Indicator titration	Amalgamation	Vacuum, 5×10^{-5} torr
		.95	19	Indicator titration	Amalgamation	Vacuum, 5×10^{-5} torr
	P-39	0.88	23	Indicator titration	Amalgamation	Vacuum, 5×10^{-5} torr
		.94	26	Indicator titration	Amalgamation	Vacuum, 5×10^{-5} torr
F	P-8	0.312	20	Atomic absorption for potassium	Amalgamation	Monitored argon gas atmosphere
		.542	23			
		1.13	22			
		.279	24	↓		↓
		.517	22			
		.947	23			
	P-34	0.278	16	Atomic absorption for potassium	Amalgamation	Monitored argon gas atmosphere
		.631	14			
		1.22	15			
		.330	17	↓		↓
		.555	15			
		1.17	16		↓	

[a]Value reported by analyst as doubtful.

Laboratory	Sample tube	Sample weight, g	Oxygen, ppm	Analytical method		Analytical environment
				End-point determination of potassium oxide	Separation	
G	P-2	(b)	(b)	(b)	(b)	(b)
H	P-3	2.14	$^a30$	Indicator titration	Amalgamation	Vacuum, 2×10^{-6} torr
			$^a20$	Flame photometry		
		2.12	$^a62$	Indicator titration		
			$^a37$	Flame photometry	↓	↓
	P-29	2.16	$^a18$	Indicator titration	Amalgamation	Vacuum, 2×10^{-6} torr
			$^a15$	Flame photometry		
		2.57	$^a18$	Indicator titration		
			$^a17$	Flame photometry	↓	↓
I	P-7	2.130	17	Potentiometric titration	Amalgamation	Vacuum, 10^{-6} torr
		2.950	22	Potentiometric titration	Amalgamation	Vacuum, 10^{-6} torr
		.974	18	Potentiometric titration	Amalgamation	Vacuum, 10^{-6} torr
	P-23	2.009	22	Potentiometric titration	Amalgamation	Vacuum, 10^{-6} torr
		2.753	14	Potentiometric titration	Amalgamation	Vacuum, 10^{-6} torr
		1.127	11	Potentiometric titration	Amalgamation	Vacuum, 10^{-6} torr
J	P-18	1.630	12	Indicator titration	Amalgamation	Purified helium gas atmosphere
		2.807	12	Indicator titration	Amalgamation	Purified helium gas atmosphere
K	P-12	0.5278	9	Indicator titration	Amalgamation	Helium gas atmosphere
		.7859	8			
		1.6657	10			
		1.0526	$^a15$	↓	↓	↓
	P-28	0.5134	10	Indicator titration	Amalgamation	Helium gas atmosphere
		1.5343	8			
		1.1417	8			
		1.0670	$^a15$	↓	↓	↓
L	P-38	4.5298	15	None	Fast-neutron activation	Potassium packaged in vacuum-melted 309 stainless-steel container
M	P-11	(b)	(b)	(b)	(b)	(b)
	P-24	(b)	(b)	(b)	(b)	(b)
N	P-9	1.65	14	Potentiometric titration	Amalgamation	Purified argon gas atmosphere
		1.38	9	Potentiometric titration	Amalgamation	Purified argon gas atmosphere
		1.48	16	Potentiometric titration	Amalgamation	Purified argon gas atmosphere
	P-36	1.84	4	Potentiometric titration	Amalgamation	Purified argon gas atmosphere
		1.67	4	Potentiometric titration	Amalgamation	Purified argon gas atmosphere
		1.52	8	Potentiometric titration	Amalgamation	Purified argon gas atmosphere

[a] Value reported by analyst as doubtful.
[b] No data reported.

Laboratory	Sample tube	Sample weight, g	Oxygen, ppm	Analytical method End-point determination of potassium oxide	Separation	Analytical environment
O	P-26	(b)	(b)	(b)	(b)	(b)
	P-10	1.54	10.7	Indicator titration	Amalgamation	Vacuum, $<10^{-5}$ torr
	P-16	2.00	11.5	Indicator titration	Amalgamation	Vacuum, $<10^{-5}$ torr
	P-31	1.44	7.8	Indicator titration	Amalgamation	Vacuum, $<10^{-5}$ torr
		1.54	7.9	Indicator titration	Amalgamation	Vacuum, $<10^{-5}$ torr
P	P-20	0.9976	13	Indicator titration for potassium	Amalgamation	Argon gas atmosphere
Q	P-5	2.85	12.1	Flame spectrophotometry	Amalgamation	Argon gas atmosphere
		3.40	13.5	Flame spectrophotometry	Amalgamation	Argon gas atmosphere
		4.42	12.1	Flame spectrophotometry	Amalgamation	Argon gas atmosphere
R	P-6	2.02	[a]41	Indicator titration	Amalgamation	Argon gas atmosphere
		1.07	14	Indicator titration	Amalgamation	Argon gas atmosphere
		.58	16	Indicator titration	Amalgamation	Argon gas atmosphere
	P-32	2.05	23	Indicator titration	Amalgamation	Argon gas atmosphere
		1.06	18	Indicator titration	Amalgamation	Argon gas atmosphere
		.53	23	Indicator titration	Amalgamation	Argon gas atmosphere
S	P-4	1.09	18	Potentiometric titration	Amalgamation	Vacuum, 10^{-6} torr
		1.38	15	Potentiometric titration	Amalgamation	Vacuum, 10^{-6} torr
	P-27	1.355	15	Potentiometric titration	Amalgamation	Vacuum, 10^{-6} torr
		1.370	18	Potentiometric titration	Amalgamation	Vacuum, 10^{-6} torr
		1.380	16	Potentiometric titration	Amalgamation	Vacuum, 10^{-6} torr
T	P-13	0.84	13.7	Potentiometric titration	Amalgamation	Helium cover gas
			15.8	Flame photometry for potassium		
		1.28	12.3	Potentiometric titration		
			15.2	Flame photometry for potassium		
		1.97	11.5	Potentiometric titration		
			14.5	Flame photometric for potassium	↓	↓
	P-30	1.70	9.3	Potentiometric titration	Amalgamation	Helium cover gas
			11.4	Flame photometry for potassium		
		1.85	14.2	Potentiometric titration		
			14.9	Flame photometry for potassium	↓	↓

[a]Values reported by analyst as doubtful.
[b]No data reported.

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TABLE II. - SUMMARY OF RESULTS OF NASA-AEC ROUND ROBIN ANALYSIS FOR OXYGEN IN SODIUM (Q-SERIES)

Laboratory	Sample tube	Sample weight, g	Oxygen, ppm	Analytical method — End-point determination of sodium oxide	Separation	Analytical environment
A	Q-17	1.40	19.6	Potentiometric titration	Amalgamation	Argon gas atmosphere
		1.36	15.1	Potentiometric titration	Amalgamation	Argon gas atmosphere
		1.41	[a]32.8	Potentiometric titration	Distillation	Vacuum, 2×10^{-6} torr
		1.41	[a]32.4	Potentiometric titration	Distillation	Vacuum, 2×10^{-6} torr
		1.41	[a]30.0	Potentiometric titration	Distillation	Vacuum, 2×10^{6} torr
	Q-24	1.44	19.7	Potentiometric titration	Amalgamation	Argon gas atmosphere
		1.41	12.6	Potentiometric titration	Amalgamation	Argon gas atmosphere
		1.465	16.5	Potentiometric titration	Distillation	Vacuum, 2×10^{-6} torr
		1.465	16.1	Potentiometric titration	Distillation	Vacuum, 2×10^{-6} torr
		1.465	20.0	Potentiometric titration	Distillation	Vacuum, 2×10^{-6} torr
B	Q-14	1.29	11	Indicator titration	Amalgamation	Monitored helium gas atmosphere
		1.25	12			
		1.75	32			
		1.30	11			
		1.37	10			
		1.22	11			
	Q-27	(b)	(b)	(b)	(b)	(b)
C	Q-18	3.27	4	Flame photometry for sodium	Amalgamation	Recirculating argon gas atmosphere
		2.76	6			
		2.48	5			
		1.53	5			
		1.23	7			
D	Q-19	2.980	7.8	Indicator titration	Amalgamation	Monitored argon gas atmosphere
		1.674	7.1	Indicator titration	Amalgamation	Monitored argon gas atmosphere
		3.232	6.9	Indicator titration	Amalgamation	Monitored argon gas atmosphere
	Q-39	3.857	4.3	Indicator titration	Amalgamation	Monitored argon gas atmosphere
		1.583	3.7	Indicator titration	Amalgamation	Monitored argon gas atmosphere
		2.538	5.3	Indicator titration	Amalgamation	Monitored argon gas atmosphere
E	Q-3	1.00	[a]23	Indicator titration	Amalgamation	Vacuum, 5×10^{-5} torr
	Q-32	0.99	17	Indicator titration	Amalgamation	Vacuum, 5×10^{-5} torr
F	Q-13	0.592	12	Atomic absorption for sodium	Amalgamation	Monitored argon gas atmosphere
		.891	10			
		1.21	11			
		.654	11			
		.872	11			
		1.27	8			
	Q-33	0.679	8	Atomic absorption for sodium	Amalgamation	Monitored argon gas atmosphere
		.903	9			
		1.21	8			
		.630	8			
		.991	7			
		1.26	8			

[a]Value reported by analyst as doubtful.
[b]No data reported.

Laboratory	Sample tube	Sample weight, g	Oxygen, ppm	Analytical method		Analytical environment
				End-point determination of sodium oxide	Separation	
G	Q-16	2.24	11	Indicator titration	Amalgamation	Vacuum, 2×10^{-6} torr
			16	Flame photometry		
		1.99	15	Indicator titration	↓	↓
			17	Flame photometry		
	Q-31	3.90	33	Indicator titration	Amalgamation	Vacuum, 2×10^{-6} torr
			28	Flame photometry		
		3.86	55	Indicator titration	↓	↓
			35	Flame photometry		
H	Q-22	(b)	(b)	(b)	(b)	(b)
I	Q-6	1.18	8.4	Potentiometric titration	Amalgamation	Vacuum, 10^{-6} torr
		2.946	11.0	Potentiometric titration	Amalgamation	Vacuum, 10^{-6} torr
	Q-23	4.451	14	Potentiometric titration	Amalgamation	Vacuum, 10^{-6} torr
		2.609	[a]35	Potentiometric titration	Amalgamation	Vacuum, 10^{-6} torr
J	Q-5	3.031	3	Indicator titration	Amalgamation	Purified helium gas atmosphere
		1.868	4	Indicator titration	Amalgamation	Purified helium gas atmosphere
K	Q-2	(b, c)	(b, c)	(b, c)	(b, c)	(b, c)
	Q-35	(b, c)	(b, c)	(b, c)	(b, c)	(b, c)
L	Q-1	(b)	(b)	(b)	(b)	(b)
	Q-34	(b)	(b)	(b)	(b)	(b)
M	Q-12	(b)	(b)	(b)	(b)	(b)
	Q-28	(b)	(b)	(b)	(b)	(b)
N	Q-10	2.80	8	Potentiometric titration	Amalgamation	Purified argon gas atmosphere
		2.46	39	Potentiometric titration	Amalgamation	Purified argon gas atmosphere
		2.46	6	Potentiometric titration	Amalgamation	Purified argon gas atmosphere
	Q-36	(b)	(b)	(b)	(b)	(b)
O	Q-29	1.160	6	Indicator titration	Distillation	Vacuum, $<10^{-5}$ torr
		1.620	5	Indicator titration	Distillation	Vacuum, $<10^{-5}$ torr
		2.030	6	Indicator titration	Distillation	Vacuum, $<10^{-5}$ torr
	Q-7	0.968	10	Indicator titration	Amalgamation	Vacuum, 10^{-5} torr
		1.350	6	Indicator titration	Amalgamation	Vacuum, 10^{-5} torr
		.726	10	Indicator titration	Amalgamation	Vacuum, 10^{-5} torr
	Q-21	(b)	(b)	(b)	(b)	(b)

[a]Value reported by analyst as doubtful.
[b]No data reported.
[c]Fast-neutron activation analysis not applicable to oxygen determination in sodium.

Laboratory	Sample tube	Sample weight, g	Oxygen, ppm	Analytical method		Analytical environment
				End-point determination of sodium oxide	Separation	
P	Q-8	0.8097	3	Indicator titration	Amalgamation	Purified argon gas atmosphere
	Q-20	1.3154	<1	Indicator titration	Amalgamation	Purified argon gas atmosphere
Q	Q-38	2.44	14.2	Flame spectrometry for sodium	Amalgamation	Argon gas atmosphere
		3.17	14.0	Flame spectrometry for sodium	Amalgamation	Argon gas atmosphere
		4.55	13.5	Flame spectrometry for sodium	Amalgamation	Argon gas atmosphere
R	Q-4	2.45	31	Indicator titration	Amalgamation	Argon gas atmosphere
		1.21	31	Indicator titration	Amalgamation	Argon gas atmosphere
		.56	23	Indicator titration	Amalgamation	Argon gas atmosphere
	Q-26	2.43	49	Indicator titration	Amalgamation	Argon gas atmosphere
		1.19	50			
		.60	58	↓	↓	↓
		1.28	56			
S	Q-11	1.22	7	Potentiometric titration	Amalgamation	Purified argon gas atmosphere
		1.505	9	Potentiometric titration	Amalgamation	Purified argon gas atmosphere
		1.51	7	Potentiometric titration	Amalgamation	Purified argon gas atmosphere
	Q-30	1.47	12	Potentiometric titration	Amalgamation	Purified argon gas atmosphere
		1.595	11	Potentiometric titration	Amalgamation	Purified argon gas atmosphere
		1.24	5	Potentiometric titration	Amalgamation	Purified argon gas atmosphere
T	Q-9	1.72	14.9	Potentiometric titration	Amalgamation	Helium cover gas atmosphere
			14.4	Flame photometry for sodium		
		2.09	13.5	Potentiometric titration		
			15.8	Flame photometry for sodium		
		1.28	17.5	Potentiometric titration		
			16.3	Flame photometry for sodium		
		1.57	12.6	Potentiometric titration	↓	↓
			13.5	Flame photometry for sodium		
	Q-37	0.96	16.5	Potentiometric titration	Amalgamation	Helium cover gas atmosphere
			17.9	Flame photometry for sodium		
		1.32	16.9	Potentiometric titration		
			17.1	Flame photometry for sodium		
		1.74	17.0	Potentiometric titration		
			16.2	Flame photometry for sodium	↓	↓

TABLE III. - FACTORIAL LAYOUT OF POTASSIUM ROUND ROBIN RESULTS

[Number of data points, n = 81.]

Analytical method		Analytical environment	Tube size			
Overall	End-point determination of potassium oxide		Small, $X_1 = -1$		Large, $X_1 = +1$	
			Method of sample removal			
			Tube cut, $X_2 = -1$	Metal extruded, $X_2 = +1$	Tube cut, $X_2 = -1$	Metal extruded, $X_2 = +1$

Mercury amalgamation, $X_5 = -1$ — Titration, $X_4 = -1$ — Vacuum, $X_3 = -1$

Cell II

Laboratory					Mean value of cell, $\overline{Y}_c$, ppm
I	I	S	S	H	
Oxygen, ppm					
17	22	18	15	18	17.08
22	14	15	18	18	
18	11		16		

Cell I

Laboratory					Mean value of cell, $\overline{Y}_c$, ppm
E	E	O	O	O	
Oxygen, ppm					
19	23	10.7	11.5	7.8	15.13
26				7.9	

Large, Tube cut: (a) Large, Metal extruded: (a)

Inert gas, $X_3 = +1$

Cell III

Laboratory												Mean value of cell, $\overline{Y}_c$, ppm
A	B	D	K	N	R	T	D	K	N	R	T	
Oxygen, ppm												
15.4	14	10	9	14	14	13.7	24	10	4	23	9.3	12.67
13	16	7	8	9	16	12.3	22	8	4	18	14.2	
	11	10	10	16		11.5	23	8	8	23		

Small, Metal extruded: (a)

Cell VII

Laboratory P	Mean value of cell, $\overline{Y}_c$, ppm
Oxygen, ppm	
13	13.0

Cell VI

Laboratory J	Mean value of cell, $\overline{Y}_c$, ppm
Oxygen, ppm	
12	12.0
12	

Flame or atomic absorption, $X_4 = +1$ — Vacuum, $X_3 = -1$

Cell IV

Laboratory H	Mean value of cell, $\overline{Y}_c$, ppm
Oxygen, ppm	
15	16.0
17	

Small, Metal extruded: (a) Large, Tube cut: (a) Large, Metal extruded: (a)

Inert gas, $X_3 = +1$

Cell V

Laboratory				Mean value of cell, $\overline{Y}_c$, ppm
F	F	T	T	
Oxygen, ppm				
20	16	15.8	11.4	17.58
23	14	15.2	14.9	
22	15	14.5		
24	17			
22	15			
23	16			

Small, Metal extruded: (a)

Cell VIII

Laboratory		Mean value of cell, $\overline{Y}_c$, ppm
C	Q	
Oxygen, ppm		
10	12.1	10.95
12	13.5	
6	12.1	

Large, Metal extruded: (a)

aNo data reported for these experimental conditions.

TABLE IV. - FACTORIAL LAYOUT OF SODIUM ROUND ROBIN RESULTS

[Number of data points, n = 78.]

Analytical method		Analytical environment	Tube size				
Overall	End-point determination of sodium oxide		Small, $X_1 = -1$			Large, $X_1 = +1$	
			Method of sample removal				
			Tube cut, $X_2 = -1$		Metal extruded, $X_2 = +1$	Tube cut, $X_2 = -1$	Metal extruded, $X_2 = +1$

Vacuum, $X_3 = -1$:

Cell II					Mean value of cell, $\overline{Y}_c$, ppm	Cell I		Mean value of cell, $\overline{Y}_c$, ppm	(a)	(a)
Laboratory						Laboratory				
S	S	G	I	I		E	O			
Oxygen, ppm						Oxygen, ppm				
7	12	. 11	8.4	14	10.04	17	10	10.75		
9	11	15	11				6			
7	5						10			

Inert gas, $X_3 = +1$:

Cell III									Mean value of cell, $\overline{Y}_c$, ppm	(a)	Cell VII		Cell VI	
Laboratory											Laboratory P	Mean value of cell, $\overline{Y}_c$, ppm	Laboratory J	Mean value of cell, $\overline{Y}_c$, ppm
A	B	N	T	T	D	A	P	D			Oxygen, ppm		Oxygen, ppm	
Oxygen, ppm											1	1	3	3.50
19.6	11	8	14.9	16.5	7.8	19.7	3	4.3	11.32				4	
15.1	12	6	13.5	16.9	7.1	12.6		3.7						
	11		12.5	17.0	6.9			5.3						
	10		12.6											
	11													

Analytical method — Overall: Mercury amalgamation, $X_5 = -1$; End-point determination of sodium oxide: Titration, $X_4 = -1$.

			Cell IV		(a)	(a)	(a)
Flame or atomic absorption, $X_4 = +1$	Vacuum, $X_3 = -1$		Laboratory G	Mean value of cell, Y_c, ppm			
			Oxygen, ppm				
			16	16.5			
			17				

Cell V (Inert gas, $X_3 = +1$) | (a) | Cell VIII | (a)

Laboratory				Mean value of cell, $\overline{Y}_c$, ppm		Laboratory		Mean value of cell, $\overline{Y}_c$, ppm
T	T	F	F			C	Q	
Oxygen, ppm						Oxygen, ppm		
14.4	17.9	12	8	11.69		4	14.2	8.59
15.8	17.1	10	9			6	14.0	
16.3	16.2	11	8			5	13.5	
13.5		11	8			5		
		11	7			7		
		8	8					

Vacuum distillation, $X_5 = +1$ — Titration, $X_4 = -1$ — Vacuum, $X_3 = -1$

Cell X		Cell IX		(a)	(a)
Laboratory A	Mean value of cell, $\overline{Y}_c$, ppm	Laboratory O	Mean value of cell, $\overline{Y}_c$, ppm		
Oxygen, ppm		Oxygen, ppm			
16.5	17.53	6	5.67		
16.1		5			
20		6			

		Inert gas, $X_3 = +1$	(a)	(a)	(a)	(a)
	Flame or atomic absorption, $X_4 = +1$	Vacuum, $X_3 = -1$	(a)	(a)	(a)	(a)
		Inert gas, $X_3 = +1$	(a)	(a)	(a)	(a)

[a] No data reported for these experimental conditions.

TABLE V. - NESTED SCHEME OF DATA FROM CELL III FOR ANALYSIS OF VARIANCE

(a) Potassium. Number of effective data points, $n = 28$

Laboratories	A_1		A_2		A_3		A_4		A_5	
Laboratory designations	D		K		N		R		T	
Blocks (analyses within given tube)	B_1	B_2	B_3	B_4	B_5	B_6	B_7	B_8	B_9	B_{10}
Within-tube analyses or replications	10	24	9	10	14	4	14	23	13.7	9.3
	7	22	8	8	9	4	16	18	12.3	14.2
	10	23	10	8	16	8	--	23	11.5	----

(b) Sodium. Number of effective data points, $n = 17$

Laboratories	A_1		A_2		A_3	
Laboratory designations	A		T		D	
Blocks (analyses within given tube)	B_1	B_2	B_3	B_4	B_5	B_6
Within-tube analyses or replications	19.6	19.7	14.9	16.5	7.8	4.3
	15.1	12.6	13.5	16.9	7.1	3.7
	----	----	17.5	17.0	6.9	5.3
	----	----	12.6	----	---	---

TABLE VI. - SUMMARY OF ANALYSIS OF VARIANCE FOR OXYGEN IN POTASSIUM

[Data from cell III.]

Source of variation	Sums of squares	Degrees of freedom	Mean square	F-ratio
Laboratories	410.49	4	102.62	$F_{calc} = \dfrac{102.62}{88.67} = 1.12$, $F_{0.95}(4, 5) = 5.19$ Nonsignificant variable
Tubes within laboratories	443.34	5	88.67	$F_{calc} = \dfrac{88.67}{4.58} = 19.36$, $F_{0.95}(5.18) = 2.77$ Significant variable
Experimental error	82.49	18	4.58	--
Total	936.32	27		

TABLE VII. - SUMMARY OF ANALYSIS OF VARIANCE FOR OXYGEN IN SODIUM

[Data from cell III.]

Source of variation	Sums of squares	Degrees of freedom	Mean square	F-ratio
Laboratories	579.08	2	289.54	$F_{calc} = \dfrac{289.54}{9.46} = 30.6$, $F_{0.95}(2,3) = 9.55$ Significant variable
Tubes within laboratories	28.39	3	9.46	$F_{calc} = \dfrac{9.46}{4.63} = 2.04$, $F_{0.95}(3,11) = 3.59$ Nonsignificant variable
Experimental error	50.93	11	4.63	-------------------------------------
Total	658.40	16		

TABLE VIII. - EXPECTED VALUES

OF MEAN SQUARE

[Laboratories, A; blocks (analyses within a given tube), B; experimental error or replication error, ϵ; harmonic mean of number of observations per block (ref. 5, p. 223), $\tilde{n}$; factors A and B random.]

(a) Layout of experimental effects

Effect	A_i	B_j	$\tilde{n}$
A_i	$1 - a/A$	b	$\tilde{n}$
$B_j(A_i)$	1	$1 - b/B$	$\tilde{n}$
$\epsilon(AB)$	1	1	$\tilde{1}$

(b) Components of variance

Variance	Expected values of mean squares
MS_A	$\sigma_\epsilon^2 + (1 - b/B)\tilde{n}\sigma_{B(A)}^2 + b\tilde{n}\sigma_A^2$
$MS_{B(A)}$	$\sigma_\epsilon^2 + \tilde{n}\sigma_{B(A)}^2$
$MS_{\epsilon(AB)}$	σ_ϵ^2

TABLE IX. - DISTANCE FROM ALKALI-METAL INLET TO TUBES

Tube	Distance, cm	Tube	Distance, cm	Tube	Distance, cm
1	6.3	14	9.4	27	8.5
2	9.6	15	7.0	28	16.8
3	6.5	16	3.4	29	14.9
4	3.9	17	4.0	30	13.3
5	2.3	18	14.9	31	11.2
6	13.1	19	12.2	32	11.0
7	10.6	20	6.2	33	10.5
8	7.8	21	5.8	34	11.0
9	4.9	22	7.1	35	16.4
10	1.8	23	14.5	36	14.4
11	1.2	24	11.8	37	13.5
12	3.7	25	9.4	38	13.5
13	12.4	26	8.0	39	15.8

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